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Room-temperature fluorohydrogenate ionic liquids of alkylpyridinium cations and allylated quaternary cyclic ammonium cations

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Abstract

A series of fluorohydrogenate ionic liquids (FHILs), $\text{Cat}^+(\text{FH})_{2,3}\text{F}^-$ (Cat^+ : alkylpyridinium cations and allylated quaternary cyclic ammonium cations), have been prepared and characterized by measuring their physical and electrochemical properties. Viscosity and conductivity of alkylpyridinium-based FHILs increase and decrease, respectively, with increase in length of the side-chain. The FHILs of allylated cations show higher ionic conductivities than those of the corresponding propylated cations and even the ethylated cations in some cases, which is explained by difference in volumes, charge distributions and rotational freedom of the side-chains according to quantum mechanical calculations. Electrochemical windows of these FHILs are around 4 V.

Introduction

Room-temperature fluorohydrogenate ionic liquids (FHILs) which contain $(\text{FH})_n\text{F}^-$ anion (bifluoride ion for $n = 1$, μ -fluoro-bis(fluorohydrogenate) ion for $n = 2$ and μ -fluoro-tris(fluorohydrogenate ion for $n = 3$) have attracted much attention because of their high ionic conductivities (100 mS cm^{-1} at 298 K for $\text{EMIm}(\text{FH})_{2.3}\text{F}$, $\text{EMIm}^+ = 1\text{-ethyl-3-methylimidazolium}$).^{1,2} Electrochemical applications such as fuel cells^{3,4} and electric double-layer capacitors⁵ are now being investigated using FHILs. Furthermore, since the handling of these systems is much easier than that of hydrogen fluoride, they are also applicable to fluorination reagents and solvents not only for preparation of organic compounds⁶⁻⁸ but also for that of fluoro-anion ionic liquids such as EMImBF_4 and EMImPF_6 with high purity.⁹ Very recently, a new synthetic route of FHILs starting from corresponding alkyl amine and dimethylcarbonate has been reported.¹⁰ Recent work has investigated application of FHILs as propellants for ion engines^{11,12} and as electrolytes for the electrolytic production of porous silicon.^{13,14}

The authors have already reported some fundamental studies on the physical and chemical properties, electrochemical stabilities¹⁵⁻²⁰ and structural characteristics²¹⁻²³ of FHILs especially composed of alkylated cyclic ammonium cations. In the series of studies, it was revealed that many quarternary cyclic ammonium cations (Cat^+) form room temperature vacuum-stable FHILs with essentially identical ratios of anion mixing. The molar ratio of the fluorohydrogenate anions, $(\text{FH})_2\text{F}^- : (\text{FH})_3\text{F}^-$, is $7 : 3$, giving a formula of $\text{Cat}^+(\text{FH})_{2.3}\text{F}^-$. It has not been clarified yet why many (but not all) alkylated cyclic ammonium cations stabilize fluorohydrogenate anions with a

particular composition while the others do not, losing HF to give solids under vacuum. On the other hand, their physical and chemical properties are strongly affected by the structure of the cation including the alkyl side-chain presumably due to the difference in the coulombic interaction with fluorohydrogenate anions and van der Waals interaction between the cations. Systematic investigation and accumulation of the data are necessary to understand the effects of the cationic structure of FHILs on their low viscosity and high ionic conductivity.

In this study, FHILs composed of *N*-alkylpyridinium (RPy⁺, R = ethyl (E), propyl (P) and *n*-butyl (B)) and allylated heterocyclic cations (*N*-allylpyridinium (AP⁺), *N*-allyl-*N*'-methylimidazolium (AMIm⁺) *N*-allyl-*N*-methylpyrrolidinium (AMPyr⁺), *N*-allyl-*N*-methylpiperidinium (AMPip⁺) and *N*-allyl-*N*-methylmorpholinium (AMMor⁺) shown in Fig. 1) have been prepared. Their physical and chemical properties and electrochemical windows are investigated and compared with those of the FHILs previously reported.

Experimental

Synthesis and Measurements.

All the reagent-grade materials used in the present study were purchased from Wako Chemical or Aldrich. The quarternary ammonium chlorides were prepared by alkylation/allylation of the corresponding amines (pyridine, *N*-methylimidazole, *N*-methylpyrrolidine, *N*-methylpiperidine and *N*-methylmorpholine), then the obtained chlorides were purified by recrystallization from acetonitrile/ethylacetate and dried under vacuum at 80°C.¹⁶ FHILs were synthesized according to the previous report.¹⁶ The obtained ionic liquids were characterized by ¹H-NMR and ¹⁹F-NMR

(Varian Mercury-300BB or Varian Gemini-300BB), gravimetry and elemental analysis. No impurities of halides were detected by addition of silver nitrate solution. Water contents in the FHILs measured by Karl Fisher titration was under 10 ppm. Measurements of thermal, physical and electrochemical properties were performed in the same way as previously reported.¹⁷

Electronic structure calculations.

Geometries were optimized to C_1 symmetry at the HF, B3LYP, PBE1PBE, MPW1PW91, and MP2 levels of theory using the program Gaussian 03.²⁴ The cc-pVTZ basis set implemented in Gaussian 03 was utilized for all elements. Natural population analyses (NPA) were performed for the B3LYP optimized local minima.²⁵

Results and discussion

Physical properties of FHILs.

All the vacuum-stable FHILs obtained in this study possess melting temperatures below 25°C. According to the elemental analysis, their formula were represented by $\text{Cat}(\text{FH})_{2.3}\text{F}$, the same stoichiometries reported for previous FHILs.^{1,2} The formula, $(\text{FH})_{2.3}\text{F}^-$, denotes mixing of $(\text{FH})_2\text{F}^-$ and $(\text{FH})_3\text{F}^-$ in the molar ratio of 7 to 3.

Thermal properties of these FHILs are summarized in Table 1 with those for the other FHILs previously reported for comparison (see Table 1 for abbreviation of the previously reported FHILs). Most of the FHILs, except for $\text{APy}(\text{FH})_{2.3}\text{F}$ and $\text{AMPyr}(\text{FH})_{2.3}\text{F}$, show super-cooled states somewhere in the temperature range of -130 to 25°C in the cooling process without

showing signals of freezing and other phase transition in the DSC measurement.

Table 1 also shows the densities (ρ), viscosities (η) and ionic conductivities (κ) of FHILs in the sequence of their cationic structures and molecular weight. The density of pyridinium-based FHILs decreases with the increase of molecular weight, which is explained by the increase of free volume in the liquid by the introduction of bulky alkyl or allyl group on the cation attenuating coulombic interaction with fluorohydrogenate anions. In general, the viscosity of *N*-alkylpyridinium FHIL, RPy(FH)_{2.3}F, increases with the extension of the *n*-alkyl side-chain on the cation as is found in the case of other FHILs.^{16,18} However, in the case of APy(FH)_{2.3}F, the viscosity of this liquid, 5.3 mPa s at 25°C, is the lowest in the series of pyridinium-based FHILs and is close to that of EMIm(FH)_{2.3}F (4.9 mPa s at 25°C). Furthermore, FHILs based on allylated cations, AMIm(FH)_{2.3}F, AMPyr(FH)_{2.3}F and AMPip(FH)_{2.3}F, provide lower viscosities than those of the corresponding propylated cations containing the same number of carbons as well.

The ionic conductivity of *N*-alkylpyridinium FHILs monotonously decreases with the extension of *n*-alkyl side-chain on the cation as a result of the increase of their viscosity. APy(FH)_{2.3}F shows the highest ionic conductivity in the series of pyridinium-based FHILs. The ionic conductivities of AMPyr(FH)_{2.3}F and AMPip(FH)_{2.3}F are 78 and 63 mS cm⁻¹, respectively, remarkably higher than both the corresponding ethylated and propylated salts. However, the ionic conductivity of imidazolium-based FHILs decreases in the order of EMIm(FH)_{2.3}F > AMIm(FH)_{2.3}F > PMIm(FH)_{2.3}F, indicating the smaller effect on the ionic conductivity by the introduction of allyl group on the cation. The plot of the molar conductivities of FHILs, λ , is shown in Fig. 2 as a function of the reciprocal viscosity, η^{-1} , in the logarithmic scale. The plots

are crowded around the ideal Walden product line determined for KCl aqueous solution, suggesting that ionic conduction of FHILs roughly obeys Walden's rule;

$$\lambda \cdot \eta = \text{constant} \quad [1]$$

The ionic conductivities of these ILs are concluded to be directly governed by the fluidity of the liquids.

Electrochemical stability.

Figure 3 shows the electrochemical windows of the FHILs. Anode and cathode limit potentials were determined as the potentials of a glassy carbon electrode where the absolute values of the current densities exceed 0.5 mA cm^{-2} at the scan rate of 10 mV s^{-1} in the linear sweep voltammetry. The anodic stability of FHILs based on aliphatic cations seems to be higher than those of aromatic cations, while the cathode limit potential of FHILs except for pyridinium group were approximately the same, probably because the cathode reaction is attributable to the reduction of the fluorohydrogenate anions to evolve hydrogen gas. The slight dependence of the cathode limit on the cationic structure would be derived from the overpotential for hydrogen gas evolution. The electrochemical window of APy(FH)_{2.3}F determined using a platinum working electrode is also shown in Fig. 3. The small overpotential for hydrogen gas evolution on the platinum electrode leads to the higher cathode limit potential. The reaction at the cathode limit of pyridinium salts with short alkyl side-chain is probably the reductive decomposition of cations.

The electrochemical windows of FHILs with allylated cations are close to those of the corresponding ILs with alkylated cations, exhibiting little effect of the introduction of allyl group on the electrochemical stabilities.

Computational results.

In order to investigate the effect of the substitution of propyl group with allyl group in the present cations, quantum mechanical calculations were performed for imidazolium-based cations. The electronic structures of EMIm⁺, AMIm⁺, and PMIm⁺ were optimized starting from C₁ symmetries and resulted in stationary points with all real frequencies (Fig. 4). Since all the levels of theory (HF, MP2, B3LYP, PBE1PBE, and MPW1PW91) gave similar optimized geometries and the details on the geometries are not the points in question here, only the dihedral angles calculated at B3LYP/cc-pVTZ are briefly summarized in this paper (see ref. 26). Table 2 lists the ionic volumes for the optimized structures of the cations calculated at different levels of theory. Table 3 lists the Mulliken and NPA charges of the cations calculated for the B3LYP optimized structures. According to the present calculations, the difference in volume does not seem to be only the reason in the higher conductivity of allylated cation-based ionic liquids than propylated cation-based ionic liquids, although the results depend on the calculation methods. This is also supported by the fact that some allylated cation-based FHILs show higher conductivities than those for the corresponding ethylated cation-based FHILs in spite of their larger ionic volumes. Besides the difference in freedom of rotation, the substitution of a propyl group with an allyl group also causes the changes in electron distribution on the cation. The atomic charges of the

hydrogen atoms in the side-chain are increased from propyl group to allyl group, especially for those on the terminal carbon, C9, whereas the atomic charges of the imidazolium ring and the C6 methyl group are unchanged. These results suggest that the substitution of allyl group for propyl group changes the ion-ion interaction involving the side-chain in the ionic liquids, including both the cation-anion and cation-cation interactions. These differences facilitate dissociation of ionic liquids and result in the lower viscosity and higher conductivity for the cases of allylated cations than those of propylated cations.

Conclusion

A new series of FHILs based on allylated quaternary cyclic ammonium cations and alkylpyridinium cations were synthesized. FHILs with allylated cations show lower viscosities and higher ionic conductivities than those with the corresponding propylated cations, which results from several factors such as the differences in size, charge distribution and rotational freedom. The good agreement of ionic conductivities and viscosities of the present FHILs with Walden's rule suggests the normal migration of ionic species governs the conduction mechanism in these systems. The electrochemical stabilities of the FHILs with allylated cations are similar to those with alkylated cations. Work on the application of these FHILs in electric double layer capacitors and in fuel cells is ongoing.

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26. C2–N3–C7–C8, 104.3° for EMIm⁺; C2–N3–C7–C8, 35.2° and N3–C7–C8–C9, –119.1°, for AMIm⁺; C2–N3–C7–C8, 101.7° and N3–C7–C8–C9, 179.7° for PMIm⁺. For EMIm⁺ and PMIm⁺, the profile of torsion energy was obtained by increasing the C2–N3–C7–C8 dihedral angle with a step of 10° at HF level. For AMIm⁺, a similar procedure was used by increasing both the C2–N3–C7–C8 and N3–C7–C8–C9 dihedral angles with a step of 20° at HF level. The geometries were fully optimized at each level from the initial structures obtained above.

Table 1 Physical properties of selected fluorohydrogenate ionic liquids.

System	M.W. / g mol ⁻¹	T_m / K	T_g / K	ρ / g cm ⁻³	η / mPa s	κ / mS cm ⁻¹	Ref.
EPy(FH) _{2.3} F	173	-	165	1.13	10.1	71	This work
APy(FH) _{2.3} F	185	203	-	1.12	5.3	82	This work
PPy(FH) _{2.3} F	187	-	-	1.11	12.3	48	This work
BPy(FH) _{2.3} F	201	-	-	1.09	29.7	25	This work
AMIm(FH) _{2.3} F	188	-	-	1.11	5.5	90	This work
AMPyr(FH) _{2.3} F	191	201	-	1.05	8.5	78	This work
AMPip(FH) _{2.3} F	205	-	-	1.06	16.7	63	This work
AMMor(FH) _{2.3} F	207	-	-	1.16	34.6	35	This work
EMIm(FH) _{2.3} F	176	208	148	1.13	4.9	100	16
PMIm(FH) _{2.3} F	190	-	152	1.11	7.0	61	16
EMPy(FH) _{2.3} F	179	-	-	1.07	9.9	74.6	17
PMPyr(FH) _{2.3} F	193	-	-	1.05	11.2	58.1	17
EMPip(FH) _{2.3} F	193	217,237	-	1.07	24.2	37.2	17
PMPip(FH) _{2.3} F	207	-	164	1.06	33.0	23.9	17

M.W.: molecular weight, T_m : melting point, T_g : glass transition temperature, ρ : density, η : viscosity, κ : conductivity, EMIm⁺: *N*-ethyl-*N'*-methylimidazolium, PMIm⁺: *N*-methyl-*N'*-propylimidazolium, EMPyr⁺: *N*-ethyl-*N*-methylpyrrolidinium, PMPyr⁺: *N*-methyl-*N*-propylpyrrolidinium, EMPip⁺: *N*-ethyl-*N*-methylpiperidinium, PMPip⁺: *N*-methyl-*N*-propylpiperidinium.

Table 2 Calculated ionic volumes ($\text{\AA}^3$) for the optimized geometries of AMIm⁺, AMIm⁺, and PMIm⁺

	B3LYP ^a	PBE1PBE ^a	MPW1PW91 ^a	MP2 ^a
EMIm ⁺	156	152	144	157
AMIm ⁺	173	158	180	178
PMIm ⁺	188	186	169	178

^aThe cc-pVTZ basis set was used.

Table 3 Mulliken and NPA charges for the optimized geometries of EMIm⁺, AMIm⁺, and PMIm⁺ at B3LYP/cc-pVTZ^a

EMIm ⁺														
	M	N		M	N		M	N		M	N		M	N
N1	0.03	-0.28	C2	0.02	0.25	N3	0.03	-0.28	C4	-0.07	-0.03	C5	-0.06	-0.03
C6	-0.18	-0.37	C7	-0.12	-0.18	C8	-0.27	-0.59	H2	0.19	0.24	H4	0.18	0.25
H5	0.18	0.25	H6a	0.13	0.22	H6b	0.15	0.23	H6c	0.15	0.23	H7a	0.13	0.21
H7b	0.15	0.22	H8a	0.12	0.21	H8b	0.12	0.24	H8c	0.14	0.21			
AMIm ⁺														
	M	N		M	N		M	N		M	N		M	N
N1	0.03	-0.28	C2	0.03	0.25	N3	0.01	-0.28	C4	-0.06	-0.02	C5	-0.06	-0.03
C6	-0.18	-0.37	C7	-0.08	-0.21	C8	-0.15	-0.24	C9	-0.24	-0.30	H2	0.19	0.25
H4	0.18	0.25	H5	0.18	0.25	H6a	0.13	0.22	H6b	0.15	0.23	H6c	0.15	0.23
H7a	0.15	0.22	H7b	0.14	0.23	H8	0.16	0.21	H9a	0.14	0.20	H9b	0.16	0.22
PMIm ⁺														
	M	N		M	N		M	N		M	N		M	N
N1	0.03	-0.28	C2	0.02	0.25	C3	0.03	-0.28	C4	0.07	-0.03	C5	-0.06	-0.03
C6	-0.18	-0.37	C7	-0.12	-0.18	C8	-0.17	-0.38	C9	-0.29	-0.58	H2	0.18	0.24
H4	0.18	0.25	H5	0.18	0.25	H6a	0.13	0.22	H6b	0.15	0.23	H6c	0.15	0.23
H7a	0.13	0.21	H7b	0.14	0.22	H8a	0.12	0.20	H8b	0.12	0.20	H9a	0.11	0.20
H9b	0.13	0.23	H9c	0.11	0.20									

^a Atom numbering schemes are shown in Fig. 4. M: Mulliken charge, N: NPA charge.

Figure captions

Fig. 1 Molecular structures of *N*-heterocyclic cations employed in this study (R = ethyl, propyl and butyl).

Fig. 2 Walden plot for FHILs obtained in this study (●) and other FHILs and typical ionic liquids (□). The dotted line indicates the ideal Walden behavior. TFSI: bis(trifluoromethylsulfonyl)amide, Tf: triflate.

Fig. 3 Potential windows of the FHILs using a glassy carbon electrode. The potential is described on the basis of the standard potential of the ferrocene(Fc)/ferrocenium(Fc^+) redox couple in each system. $\text{APy}^+(\text{Pt})$ denotes the electrochemical window of $\text{APy}(\text{FH})_{2,3}\text{F}$ using a platinum electrode.

Fig. 4 Optimized structures of (a) EMIm^+ , (b) AMIm^+ , and (c) PMIm^+ at B3LYP/cc-pVTZ and their atom numbering schemes.

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Fig. 4 Optimized structures of (a) EMIm⁺, (b) AMIm⁺, and (c) PMIm⁺ at B3LYP/cc-pVTZ and their atom numbering schemes.